Synthesis of Silica-Potassium-Nitrogen from Carbamide and Potassium Silicate by CO 2 Precipitator

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Synthesis of Silica-Potassium-Nitrogen from Carbamide and Potassium Silicate by CO_2 Precipitator

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Abstract. Potassium silicate is well known as a fertilizer and source of silica for plants growth. This study aims to infiltrate nitrogen from carbamide (urea) into potassium silicate solution to produced silica potassium nitrogen (Si-K-N) matrix by precipitation method using CO_2 as precipitator. Potassium silicate in the range of 3-8% SiO_2 was obtained by extracting silica from geothermal sludge using potassium hydroxide solution. Carbamide is added to the potassium silicate solution allowed by mixing and flowing of CO_2 gas in reactor glass. The result of IR spectra indicated the presence of N-H groups, potassium and silica in the gel matrix produced from precipitation process while no N-H group appears in the gel matrix produced from precipitation in the absence of carbamide. X-ray fluorescence showed the composition of the product Si-K-N in the range of 40 to 50 %SiO_2 and in the range of 50 to 60 %K_2O.

Introduction

The production of silica from sodium silicate by the precipitation method produces two types of products namely precipitated silica and silica gel. The factors affecting in the precipitation method include raw concentration (usually alkaline silicate), pH value and type of acid or salt catalyst used [1]. The monomeric form of silica (Si-OH) will be polymerized to form primary particles and then flocculated to produce precipitate silica or it undergoes polymerization (gelation) where the polymer chain combines to produce silica gel. The synthesis of silica gel matrix that has been studied previously also follows the polymerization step by combining several elements to form composites [2]. In addition to acid catalysts, CO_2 can also be used to produce silica precipitates from alkaline silicate solutions [3].

Silica gel and precipitated silica have different characters so that the application of both silica products is also different. One of the applications developed was amine grafted silica which was applied as an adsorbent to capture CO_2. Amine grafts in silica pass through several stages of the process which are quite difficult and of considerable cost [4,5]. This study develops silica-potassium-nitrogen composites from potassium silicate and carbamide (urea) by precipitation method in the presence of CO_2. Urea, also known as carbamide, is an organic compound with chemical formula $CO(NH_2)_2$. This amide has two $-NH_2$ groups joined by a carbonyl (C=O) functional group. Umegaki et al [1] reported the fabrication of spherical silica from sodium metasilicate solution using urea as a precipitant where homogeneity of the silica particles was improved by adjusting the ratio of sodium metasilicate to urea. Nasr and Taylor [6] investigated the gelation mechanism and kinetics of the silicate / urea system in detail including hydrolyzed urea solutions at high temperatures where the product starts gelation. It was also reported that the gelation speed depends on temperature, sodium silicate concentration, urea concentration, and salt concentration [1,6,7]. Urea is not acidic or alkaline in water under ambient conditions but produces ammonia in water during heating so that the solution becomes alkaline. On the other hand, urea solution can dissolve silica at high temperatures in a controlled manner [7]. By using CO_2, the research developed can be done at room temperature and without adding acid or salt for the purposes of the gelation process.

The sodium silicate or potassium silicate solution is alkaline so that the use of acid will reduce the acidity at several pH values where silanol (Si-OH) or silicic acid and salt are formed, which are different at each pH. That's why the character of silica gel is different at different pH value. The purpose of this study was to study the effect of urea on the characterization of silica-potassium-nitrogen composites by precipitation method. The use of CO_2 in this study aims to control the pH of the solution by the formation of carbonic acid during the precipitation process. This composite can be applied as fertilizer not for adsorbents so that it does not require a large surface area. However, studies are still being developed for more applications.

Materials and Methods

Silica source from geothermal sludge obtained from the geothermal plant. potassium hydroxide (KOH) as solvent on silica extraction obtained from CV. Bratachem Surabaya and Urea obtained from CV Medica Vanjaya Surabaya.

Geothermal was grinded to a size about 80-100 mesh and analyzed for its silica content. The chemical composition of geothermal sludge by XRF analyze was SiO2: 93%, CaO: 3.03%, K_2O 2.02%. The extraction of silica prepared by extraction of 300g geothrmalsludge using 1L of sodium hydroxide (KOH) 5 N solutions at 95°C for 1.5 h to produce the potassium silicate solution. The potassium silicate solution was analyzed for the content of potassium oxide (K_2O) with AAS method and analyzed of silica content (SiO2) by spectrofotometry method. The result showed that sodium silicate solution was has a silica concentration of 11.85 % and sodium oxide concentration of 10.57 %. Sodium silicate solution was then dilution by demineralized water in the range ratio of 1:1; 1:2; 1:3; 1:4; and 1:5 obtained the concentrations of 7.8; 6.5; 5.5; 4.7 and 3.1% SiO_2 by stoichiometry calculation method. The amount of carbamide used in this study is quite large, namely 50 g and 75 g, both of which are dissolved in 1L potassium silicate solution, with the hope that the Si-K-N composite gel produced contains the adequate of nitrogen component.

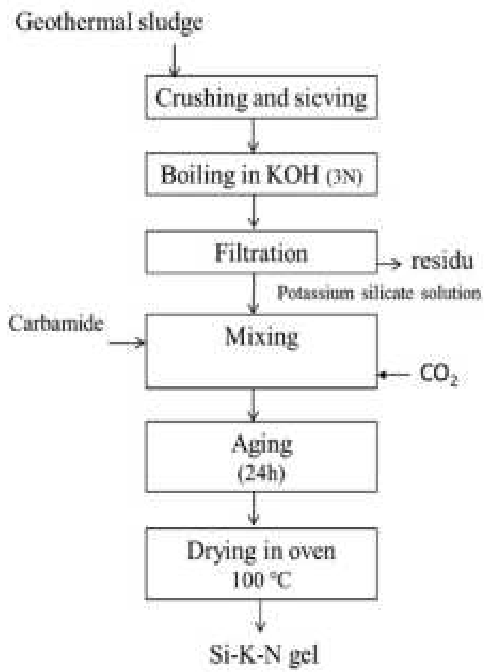


Fig. 1. Diagram procedure of Si-K-N gel.

The flow diagram of procedure of Si-K-N gel preparation showed in Fig.1. Potassium silicate solution was added with a carbamide in a 2000-mL reactor glass with stirring then carbon dioxide was injected from the CO_2 reservoir into the reactor at a rate of 1 L / h until the suspension was formed. The suspension from the reactor was aged for 24 hours then dried in an oven of 100 C for 24 hours. The dry gel was crushed and sieved into about 100 mesh for analysis purposes.

The Si-K-N product analyzed by X-ray fluorescence (XRF), Scanning electron microscopy with energy diffraction x-ray (SEM-EDX) and Fourier transform infrared spectroscopy (FTIR).

Results and Discussions

Fig. 2 showed the IR spectra of Si-K-N product prepared without carbamide and with the addition of 75g/L carbamide solution. The IR spectra on Si-K-N products prepared by 75 g of carbamide showed a change in intensity in the area of about 3700-2500 cm^{-1} which is characteristic of the silane (Si-OH) group. Stretching modes N-H or $-NH_2$ which is a condensed amine group indicated by the presence of a wideband at wavenumber around 3150 to 3500 cm^{-1}. The OH group was replaced by the N-H group which indicated the role of carbamide in the formation of Si-K-N composites. The bands at 1624 shows the presence of groups C = N, 1394 and 1291 cm^{-1} shows the presence of groups C = O, CH and CH_2 respectively, while in the band around 1000 cm^{-1} attribute to siloxane (Si-O-Si) which binds to potassium.

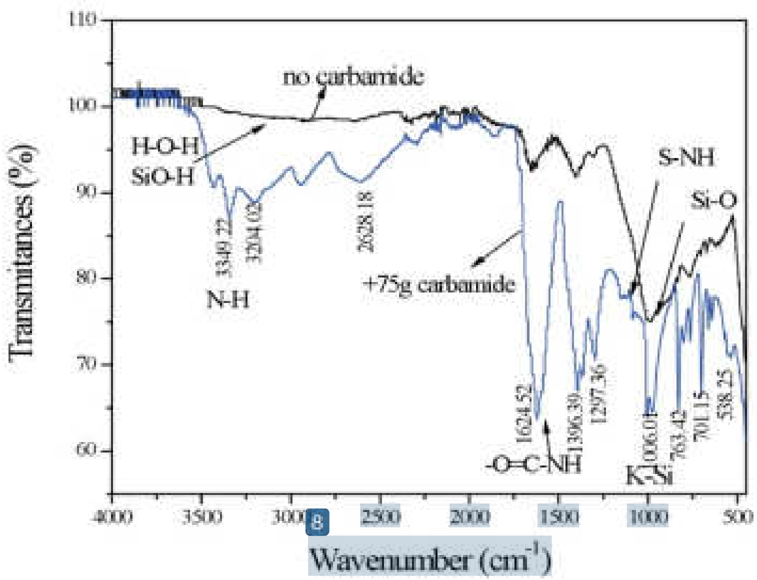
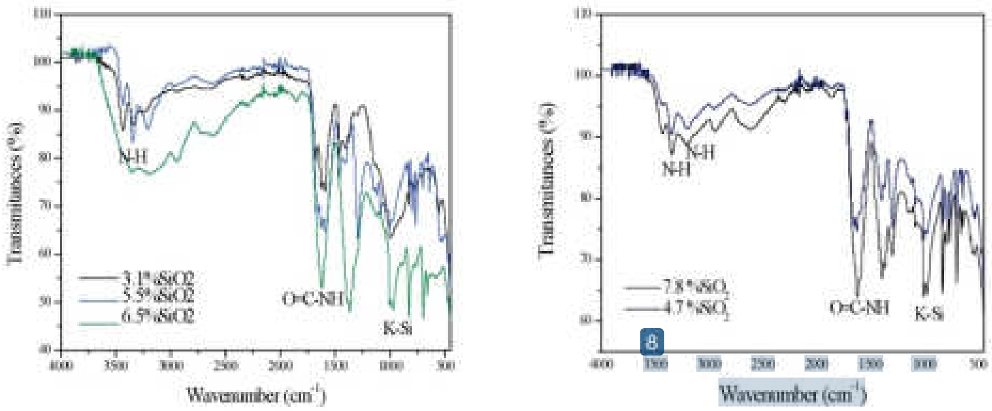


Fig. 2 The IR spectra of Si-K-N product prepared without carbamide and with the addition of 75g/L carbamide solution.

Fig. 3 showed the IR spectra for some silica concentrations from 3.1% to 7.8% SiO_2. The greater the concentration of silica, the absorption intensity increases at each functional group. The stretching band seems to be increasingly sharp especially attribute to the N-H group (wave numbers 3150 to 3500 cm^{-1}), C = O-NH (1624 cm^{-1}) and siloxan (1006 cm^{-1}). This shows that the greater the silica, the greater the formation of N-H and K-Si groups. Conversely, the addition of carbamide concentrations from 50 g to 75 g indicates an decreasingly of stretching bands as shown in Fig. 4.



(a) (b)

Fig. 3 IR spectra Si-K-N samples prepared by silicate concentration in the range of 3.1% to 7.8% SiO_2 .

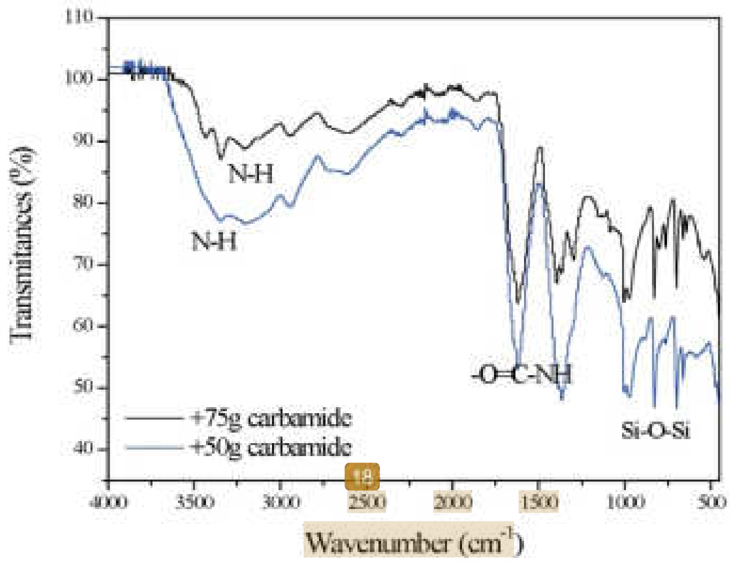


Fig. 4 IR spectra Si-K-N prepared by addition of 50 g and 75 g of carbamide.

Fig. 5 showed the SEM image of Si-K-N particles prepared by a) without carbamide, b) addition of 50g of carbamide and c) addition of 75 g of carbamide. The addition of carbamide tends to make particles coalesce to form larger lumps. Gel formed after the aging process shows the ability of CO_2 as a precipitator as well as determines the acidity of the solution where polymerization can occur to form aggregates. CO_2 as a precipitator usually acts to produce silica deposits from alkaline silicates but in the case of silicate acidification in the presence of carbamide leads to gel formation.

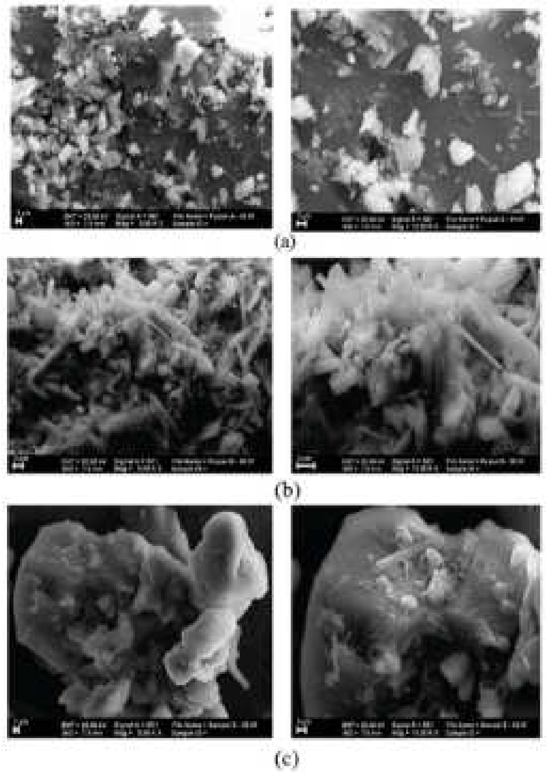


Fig. 5 SEM image of Si-K-N particles prepared by a) without carbamide, b) addition of 50g of carbamide and c) addition of 75 g of carbamide.

Fig. 6 showed the composition of Si-K-N product by X-ray fluorescence analysis. The Si-K-N product contains silica (SiO_2) 40-50 % and potassium oxide 50-60%. The presence of nitrogen in the product was not detected via x-ray but can be identified through IR spectra as described previously. The Si-K-N gel is a mixture and reaction of silicate potassium and carbamide CO $(NH_2)_2$ where nothing is wasted as an unconverted material. The greater the concentration of silica in the material then the composition of the silica in the product is also greater, so to get the composition of the product it can be done with the setting of raw concentration.

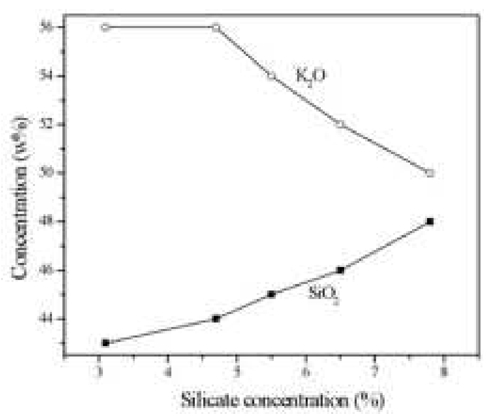


Fig. 6 The composition of Si-K-N gel product.

Summary

Silica potassium nitrogen (Si-K-N) matrix gel have been produced from potassium silicate solution and carbamide succesfully by precipitation method using CO_2 as precipitator. The CO_2 gas can reduce pH of the solution and gel formation. The nitrogen from carbamide can form composites through gel formation, and the composition of raw material or the ratio of silica and potassium oxide will affect the composition of product.

References

[1] T. Umegaki, Y.E. Nomoto, Y.K. Ojima, Fabrication of Spherical Silica Particles from Sodium Silicate and Their Application as Support Materials for Ruthenium based Catalysts for the Hydrogenation of Supercritical Carbon Dioxide into Formic Acid, J. Japan Inst. of Ene., 96 (2017) 332-338.

[2] S. Muljani, Synthesis of matrix of SI-K-HAs gel from geothermal sludge and peat, Reaktor 18:2 (2018) 76-70.

[3] R. Dewati, Suprihatin, K. Sumada, S. Muljani, Precipitated silica from pumice and carbon dioxide gas $(CO)_2$ in bubble column reactor J. of Physics. Conf. (2018) 1-5.

[4] E. G. Moschetta, M. A. Sakwa-Novak, J. L. Greenfield, C. W. Jones, Post grafting amination of alkyl halide-functionalized silica for applications in catalysis, adsorption and spectroscopy, Langmuir, 31:7 (2015) 2218–2227.

[5] W. Conway, X. Wang, D. Fernandes, R. Burns, G. Lawrance, M. Maeder, Toward rational design of amine solutions for PCC applications: the kinetics of the reaction of $CO_2(aq)$ with cyclic and secondary amines in aqueous solution, Env.Sci.Tech. 46:13 (2012) 7422-7429.

[6] H.A.Nasr-El-Din, K.C.Taylor, Evaluation of sodium silicate/urea gels used for water shut-off treatments, J. Petrol.Sci and Eng. 48 (2005) 141-160.

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